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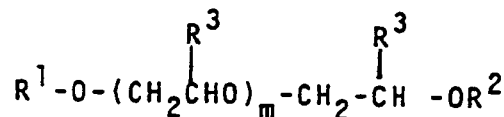
(54) **Flowable graft and derivatized polymer concentrate and lubricant containing same.**

(57) The bulk viscosity of an oil additive concentrate which comprises:

(a) a mineral oil of lubricating viscosity, and

(b) from 5 to 35 weight percent, based on (a) + (b), of a graft and derivatized polymer, can be reduced from a value above 2000 centistokes by incorporating a minor amount of a co-solvent having the formula:

a)



or

b)  $R^4O-CO-CH_2-(CH_2)_n-COOR^4$

wherein  $R^1$  and  $R^2$ , which can be the same or different, each represents hydrogen or a  $C_1 - C_{25}$  hydrocarbon group,

$R^3$  represents hydrogen or a  $C_1 - C_{25}$  hydrocarbon group,

each  $R^4$  represents a  $C_1 - C_{12}$  hydrocarbon group,

$m$  is 0 to 25, and

$n$  is 0 to 10.

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## FLOWABLE GRAFT AND DERIVATIZED POLYMER CONCENTRATE AND LUBRICANT CONTAINING SAME

This invention relates to a multi-functional graft and derivatized polymeric additive composition which is useful as a dispersant, viscosity index improver, and anti-oxidant in lubricating oils. More particularly, the invention relates to flowable concentrates of the multi-functional polymeric additive and to a method for their preparation.

Multi-functional graft and derivatized polymers or copolymers for lubricating oil compositions are well known. In general, a hydrocarbon solution of a polymer substrate, for example a copolymer, terpolymer or higher polymer as graft base, is reacted with an olefinic carboxylic material in a graft reaction to prepare a grafted polymer. This is then further functionalized by a reaction with a variety of compounds to produce an oil concentrate of the multi-functional polymeric additive. The oil concentrate will generally contain from 5 to 35 weight percent of the multi-functional polymeric additive based on the total weight of the mixture. Ethylene copolymers which have been grafted with maleic anhydride and then functionalized with an amine compound represent one class of multi-functional lubricant additive. Examples of grafted and derivatized multi-functional additives may be seen in US-A-4146489, US-A-4114181 and US-A-4089794.

A serious problem, which has been encountered with oil concentrates of certain high molecular weight grafted and derivatized polymers and copolymers, is their very high bulk viscosity. Bulk viscosities, determined as the Kinetic Viscosity at 100°C, of over 2000 Centistokes have been observed relative to the identical underivatized polymer with a Kinetic Viscosity at 100°C of less than 1000 Centi stokes. Some of the graft and derivatized copolymers are so viscous that their bulk viscosity cannot be measured. The high Bulk viscosity of these product concentrates makes them extremely difficult to handle, process and/or transport, which is a serious drawback to their usefulness.

A method has now been found for substantially reducing the high bulk viscosity of oil concentrates of high molecular weight graft and derivatized polymers and copolymers greatly enhancing their usefulness as lubricant additives.

EP-A-0338672 discloses graft and derivatized copolymers and lubricating oil compositions containing them.

US-A-4707285 discloses haze-free graft and derivatized ethylene-propylene copolymers for lubricants.

US-A-4693838 discloses multi-functional viscosity index improvers for lubricants.

In accordance with this invention, it has been found that the bulk viscosity of oil concentrates of grafted and derivatized polymers/copolymers, which are generally characterized by bulk viscosities of over 2000 Centistokes at 100°C, can be substantially reduced by mixing a minor amount of a co-solvent which is an alkyl or alkaryl (poly)ethylene glycol ether or ether alcohol or ester of a diacid is effective for reducing the bulk viscosities of oil concentrates of grafted and derivatized polymers/copolymers. The co-solvent may be added directly to the finished oil concentrate of the graft and derivatized polymers/copolymers or it may be employed together with the amine used in the derivatization reaction, that is in the final step of the preparation of the grafted and derivatized polymer/copolymer.

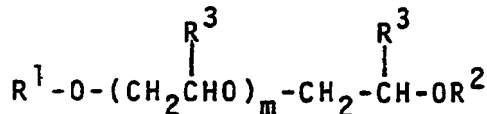
More specifically, this invention provides an oil additive concentrate which comprises:

(a) a mineral oil of lubricating viscosity, and

(b) from 5 to 35 weight percent, based on (a) + (b), of a graft and derivatized polymer.

In accordance with the invention, the bulk viscosity measured as the Kinematic viscosity at 100°C, of the concentrate is reduced from a value above 2000 Centistokes by incorporating a minor amount of a co-solvent having the formula:

a)



or

b)  $R^4O-CO-CH_2-(CH_2)_n-COOR^2$

wherein  $R^1$  and  $R^2$ , which can be the same or different, each represents hydrogen or a  $C_1 - C_{25}$  hydrocarbon group,  $R^3$  represents hydrogen or a  $C_1 - C_{25}$  hydrocarbon group, each  $R^4$  represents a  $C_1 - C_{12}$  hydrocarbon group,  $m$  is 0 to 10, and  $n$  is 0 to 10.

The graft and derivatized polymer or copolymer may be prepared from a variety of polymer or

copolymer substrates. A typical substrate can be prepared from ethylene and propylene or it can be prepared from ethylene and a higher olefin e.g. a  $C_3$  to  $C_{10}$  alpha-monoolefin. More complex polymers, often designated as interpolymers, may be prepared using three or more olefin components. In general a conventional polymerization reaction is employed to prepare the polymer.

5 The substrate may be an ethylene-propylene copolymer and may comprise 15 to 80 mole percent of ethylene and 20 to 85 mole percent propylene. Terpolymers and interpolymers which may be made up of three or more olefins may be employed as the polymer substrate. A typical terpolymer may contain from 0.5 to 10 mole percent of the terpolymer component.

10 The polymer substrate employed in the preparation of graft and derivatized polymers for lubricating oils is an oil-soluble, substantially linear, rubbery material having a number average molecular weight from 5,000 to 500,000, or even higher. Preferred are polymers having a number average molecular weight from 50,000 to 200,000, with the most preferred polymers having a number average molecular weight from 75,000 to 150,000.

15 The terms polymer and copolymer are used herein in a generic sense and are intended to encompass ethylene copolymers, terpolymers or interpolymers. These substrates may contain minor amounts of other components, so long as their basic characteristics are not materially changed.

20 An ethylenically unsaturated carboxylic acid material, such as maleic anhydride, is grafted on to the polymer substrate. These graft monomers generally contain at least one ethylenic bond and at least one, preferably two, carboxylic acid or carboxylic acid anhydride groups, or a polar group which is convertible into a carboxyl group by oxidation or hydrolysis. Maleic anhydride or a derivative thereof is the preferred graft monomer. It is grafted onto the ethylene copolymer or terpolymer to give two carboxylic acid functionalities.

25 Grafting of the ethylenically unsaturated carboxylic acid graft monomer onto the polymer may be conducted following a number of well known processes. Grafting can be effected using the "ene" process or, alternatively, by grafting it in solution or in solid form using a free-radical initiator. The free-radical induced grafting of ethylenic unsaturated carboxylic acid onto a polymer substrate may be conducted in a hydrocarbon solution of the polymer, such as in benzene. It is carried out at an elevated temperature, e.g. from 100 to 250°C, more preferably at 150 to 180°C, under an inert atmosphere. Grafting may be conducted in a mineral lubricating oil solution of the polymer.

30 The grafted copolymer is then reacted with an additional functional compound in a derivatization reaction to produce the multi-functional lubricant additive. The derivatization reaction may be carried out using a polyamine, a hydroxyamine, or a polyol. Particularly useful polyamines are those having from 2 to 20 carbon atoms and 2 to 5 nitrogen atoms in the molecule, where only one nitrogen atom is a primary nitrogen atom and all the rest are tertiary nitrogen atoms or highly hindered secondary nitrogen atoms. The class of suitable polyamines includes: hydrocarbyl polyamines including alkyl, aryl and mixed alkaryl polyamines which may contain additional groups such as hydroxy, oxyamide and imidazoline groups, N-phenyl-phenylenediamine, and N-aminoalkyl morpholine.

35 Useful hydroxyamines are those hydroxyamines having from 2 to 20 carbon atoms, 1 to 4 hydroxy groups and 1 to 5 nitrogen atoms. Typical hydroxyamines include diethanolamine, dipropanol amine, tris-hydroxymethylamino-methane and 2-amino-2-ethyl-1,3-propanediol.

40 Useful polyols for the derivatization reaction are the polyols having from 2 to 20 carbon atoms and having from 2 to 5 hydroxyl groups. Typical polyols include: glycerol, and alkylene glycols, such as dipropylene glycol and pentaerythritol.

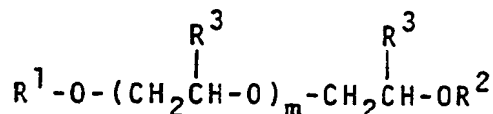
45 Certain grafted and derivatized ethylene polymers which have been prepared using a relatively high molecular weight polymer substrate are characterized by having high bulk viscosities. The bulk viscosity measure referred to is the Kinematic Viscosity in Centistokes measured at 100°C. The present invention is especially useful for grafted and derivatized polymers having bulk viscosities over 2000 Centistokes at 100°C. The value of the present invention increases as the bulk viscosity of the grafted and derivatized polymer increases and becomes dramatically effective when employed with grafted and derivatized polymers having bulk viscosities so high that their bulk viscosity generally cannot be measured in a practical way. Oil concentrates, of grafted and derivatized polymers having bulk viscosities ranging from 2000 to 5000 Centistokes, or even higher, and more generally, from 3500 to 5000 Centistokes, and above, are contemplated for treatment in accordance with this invention. A class of grafted and derivatized polymers which benefits significantly from the present invention are maleic anhydride-grafted and derivatized ethylene copolymers having bulk viscosities from 2000 to 5000 Centistokes, or higher.

55 It has been found that the high bulk viscosities of grafted and derivatized polymers may be substantially reduced, and their usefulness as lubricating oil additives can be substantially improved, if they are prepared as concentrates in admixture with co-solvents comprising high boiling alkyl or alkaryl ethylene glycol ethers

or ether alcohols and ester of diacids of formulae (a) and (b) described hereinbelow.

The polymer substrates which are used in the preparation of the grafted and derivatized polymers comprising the oil concentrates employed in the instant invention will generally have a number average molecular weight from 5,000 to 500,000, or higher. More often, the polymer substrates intended for use in preparing multi-functional lubricating oil additives will have a number average molecular weight from 25,000 to 250,000. A particularly preferred class of polymer substrates are the ethylene-propylene copolymers having a number average molecular weight from 50,000 to 200,000, with a still more preferred range being from 75,000 to 150,000.

The classes of co-solvents which are employed to produce flowable oil concentrates of the high molecular weight grafted and derivatized polymers have the general formulae: a)



in which R<sup>1</sup> and R<sup>2</sup>, which can be the same or different, each represent hydrogen or a hydrocarbon group having from 1 to 25, preferably from 1 to 12, carbon atoms and m is 0 to 25, preferably 0 to 10 and

b) R<sup>4</sup>O-CO-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>n</sub>-COOR

in which each R<sup>4</sup> represents a hydrocarbon group having from 1 to 12 carbon atoms and n is 0 to 10.

In both formulae, the hydrocarbon groups R<sup>1</sup> to R<sup>4</sup> may be alkyl groups having from 1 to 5 carbon atoms, aryl groups having from 6 to 10 carbon atoms, or alkaryl groups having from 7 to 25 carbon atoms. The preferred values for m and n are 2 to 6.

Examples of the co-solvents represented by formula 1 above include the series of compounds designated as Surfonic Surface-active agents marketed by the Texaco Chemical Company. These compounds are prepared by reacting ethylene oxide with nonyl phenol to produce compounds represented by the formula: C<sub>9</sub>H<sub>19</sub>C<sub>6</sub>H<sub>4</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>, H in which m' is from 1 to 10.

Reduction in the high bulk viscosities of the oil solution of the grafted and derivatized polymers is achieved by mixing a minor amount of the prescribed co-solvent with the copolymer. In general, an oil concentrate of the grafted and derivatized polymer containing from 5 to 25 weight percent of the grafted and derivatized polymer dissolved therein and containing from 0.1 to 5 weight percent of the co-solvent, based on the total weight of the concentrate will exhibit substantially improved flow or fluid characteristics for the concentrate mixture. A preferred amount of co-solvent in the concentrate mixture is from 0.5 to 3 weight percent, based on the total weight of the concentrate, with the most preferred concentration of the co-solvent being from 1.5 to 3 weight percent. In the method described above, a flowable concentrate is obtained by mixing an effective or suitable amount of the co-solvent into the oil concentrate of the final grafted and derivatized polymer or copolymer.

Alternatively, the flowable oil concentrate may be prepared by employing the co-solvent with the derivatizing compound before the reaction between the derivatizing compound and the grafted polymer. After the derivatization reaction has been completed, the result will be a substantially improved flowable oil concentrate of the grafted and derivatized polymer.

The following Examples illustrate the practice of this invention.

#### EXAMPLE 1

47.0 grams of a solid maleic anhydride-grafted polymer (rubber) in which the polymer substrate comprised 58 mole percent of ethylene and 42 mole percent of propylene, having a number average molecular weight of about 135,000, on which had been grafted 1.1 weight percent of maleic anhydride was dissolved at 160°C with mechanical stirring under a nitrogen blanket in 507 grams of solvent neutral mineral oil having a viscosity at 100°C of 100 SUS (20.4 cSt). After the polymer had dissolved, mixing was continued for an additional hour at 160°C.

1.1 grams of neat N-phenyl-1,4-phenylenediamine was added to the oil solution of the polymer and reaction was effected over 4 hours at 160°C under nitrogen. The reaction mixture containing the derivatized graft polymer was then cooled to 100°C and filtered. The polymer content of the oil-polymer concentrate

mixture was 8.5 weight percent.

An attempt was made to measure the Kinematic viscosity at 100° C of the grafted and derivatized polymer-oil concentrate, but it was too viscous to measure. It was estimated to have a Kinematic viscosity at 100° C of greater than 5000 Centistokes.

- 5 A variety of co-solvents were added, at 160° C for minutes, to the above-prepared grafted and derivatized polymer-oil concentrate. The co-solvents were blended into the concentrates by mixing at 160° C for 30 minutes. The viscosities of the concentrate mixtures containing the co-solvent was determined and the results are set forth in Table 1 below.

10 TABLE I

Co-Solvent Effect on the Viscosity of the Oil-Polymer Mixture of Example I		
Co-Solvent	Amount, wt.% (1)	Kin Vis @ 100° C
None	---	TVTM (2)
Jeffox PPG 2000(a)	1.8	1572
Emolien 2986(b)	2.8	1530
Surfonic N-31.5(c)	1.8	1497
Surfonic N-40(d)	1.8	1471

(1) Weight percent of co-solvent in the oil-polymer concentrate based on the total weight of the concentrate.

(2) Too viscous to measure (Kin Vis @ 100° C approx > 5000 CSt).

(a) (poly ethylene-propylene glycol).

(b) (2-ethylhexyl diester of azelaic acid).

(c) (ethoxylated nonyl phenol with 3.15 moles of ethylene oxide per mole of nonyl phenol).

(d) (ethoxylated nonyl phenol with 4.0 moles of ethylene oxide per mole of nonyl phenol).

- 35 The following Examples illustrate the preparation of the grafted and derivatized polymer wherein the co-solvent was employed during the derivation reaction.

#### 40 EXAMPLE II

- 47.2 grams of a solid maleic anhydride grafted ethylene-propylene copolymer having a number average molecular weight of about 135,000 and having 1.1 weight percent of maleic anhydride grafted thereon, was dissolved in 507 grams of the solvent neutral base oil used in Example 1 at 160° C with stirring, while being maintained under a nitrogen atmosphere. A mixture of 1.1 grams of N-phenylphenylenediamine and 10 grams of Surfonic N-31.5 was prepared at 70° C and charged to the reactor containing the oil solution of the grafted ethylene-propylene copolymer. The derivatization reaction was conducted at 160° C under a nitrogen atmosphere for 2 hours. The reaction mixture was cooled to 100° C and screen filtered through a 100 mesh (0.15 mm) screen. The bulk viscosity of the reaction mixture concentrate was 1495 Centistokes Kinematic Viscosity at 100° C, as compared to the reaction product without the addition of Surfonic N-31.5, which was too viscous to measure

#### 55 EXAMPLE II

255 grams of a solid maleic anhydride-grafted ethylene propylene copolymer having a number average molecular weight of about 135,000 and having 1.1 weight percent of maleic anhydride grafted thereon was dissolved in 2745 grams of the solvent neutral based oil at 160° C with stirring while being maintained

under a nitrogen atmosphere. A mixture of 5.0 grams of N-phenylphenylenediamine and 50 grams of Surfonic N-40 was prepared at 70°C, and charged to the reactor containing the oil solution of the grafted ethylene-propylene copolymer. The derivatization reaction was conducted at 160°C under a nitrogen atmosphere for 2 hours. The reaction mixture was cooled at 100°C and screen filtered through a 100 mesh (0.15 mm) screen. The bulk viscosity of the reaction mixture concentrate was 1229 Centistokes Kinematic Viscosity at 100°C, as compared to the reaction product without the addition of Surfonic N-40, which was too viscous to measure.

#### EXAMPLE IV

72.0 grams of a solid maleic anhydride graft ethylene-propylene copolymer having an number average molecular weight of about 80,000 and having 0.85 wt.% of maleic anhydride grafted thereon was dissolved in 528 grams of solvent neutral base oil at 160°C with stirring while being maintained under a nitrogen atmosphere. A mixture of 1.5 grams of N-phenylphenylenediamine and 10 grams of Surfonic N-31.5 was prepared at 70°C and charged to the reactor containing the oil solution of the grafted ethylene-propylene copolymer. The derivatization reaction was conducted at 160°C under a nitrogen atmosphere for about 2 hours. The reaction mixture was cooled to 100°C and filtered through a 100 mesh (0.15 mm) screen. The bulk viscosity of the reaction mixture concentrate was 1195 Centistokes Kinematic Viscosity at 100°C. The bulk viscosity of this reaction product without the addition of Surfonic N-31.5 was 2048 Centistokes Kinematic Viscosity at 100°C. This further illustrates the effectiveness of the co-solvent when used in the derivatization reaction.

#### EXAMPLE V

The oil solution of the grafted ethylene-propylene copolymer of Example IV was reacted in a derivatization reaction with a mixture of 1.5 grams of N-phenyl-phenylenediamine and 10 grams of Surfonic N-40. The reaction was conducted in the same manner as in Example IV. The bulk viscosity of the reaction mixture concentrate was 1183 Centistokes Kinematic Viscosity at 100°C.

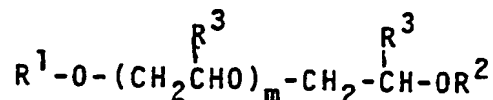
#### Claims

1. An oil additive concentrate which comprises:

(a) a mineral oil of lubricating viscosity, and

(b) from to 35 weight percent, based on (a) + (b), of a graft and derivatized polymer,

characterised in that the bulk viscosity, measured as the Kinematic viscosity at 100°C, of the concentrate is reduced from a value above 2000 centistokes by incorporating a minor amount of a co-solvent having the formula: a)



or

b)  $R^4O-CO-CH_2-(CH_2)_n-COOR^4$

wherein  $R^1$  and  $R^2$ , which can be the same or different, each represents hydrogen or a  $C_1$ - $C_{25}$  hydrocarbon group,

$R^3$  represents hydrogen or a  $C_1$ - $C_{25}$  hydrocarbon group,

each  $R^4$  represents a  $C_1$ - $C_{12}$  hydrocarbon group,

m is 0 to 10, and

n is 0 to 10.

2. An additive concentrate according to Claim 1 characterised in that the amount of co-solvent is from

0.1 to 5 weight percent, based on the weight of concentrate.

3. An additive concentrate according to Claim 1 or 2 characterised in that the co-solvent has the formula:



5 in which  $R^5$  represents an aliphatic hydrocarbon radical and  $m'$  is 1 to 5.

4. An additive concentrate according to Claim 1 or 2 characterised in that the co-solvent has the formula:



in which  $m'$  is 1 to 10.

10 5. An oil concentrate according to any one of Claims 1 to 4 characterised in that the graft and derivatized polymer has a number average molecular weight of 5000 to 500,000.

6. An oil additive concentrate according to any one of Claims 1 to 5 characterised in that the graft and derivatized polymer is an ethylene copolymer grafted with maleic anhydride and derivatized with N-phenylphenylenediamine.

15 7. A lubricating oil composition comprising a mineral oil of lubricating viscosity characterised by a minor dispersant amount of the additive concentrate according to any one of Claims 1 to 6.

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# EUROPEAN SEARCH REPORT

Application Number

EP 89 31 1706

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 190 869 (EXXON CHEMICAL PATENTS) * Page 5, line 17 - page 6, line 8; page 7, line 29 - page 8, line 7; page 9, line 16 - page 10, line 6; page 11, lines 1-7 * ---	1,2,5,7	C 10 M 161/00 C 10 M 157/00 C 10 M 157/04 // (C 10 M 157/00 C 10 M 145:26 C 10 M 145:36 ) (C 10 M 157/04
Y	EP-A-0 014 746 (RÖHM GmbH) * Page 7, line 15 - page 8, line 28; page 13, example 1 * ---	1,2,5,7	C 10 M 145:26 C 10 M 145:36 C 10 M 149:06 ) (C 10 M 161/00
P,X	GB-A-2 206 600 (SANYO CHEMICAL INDUSTRIES) * Page 3, line 18 - page 4, line 2; page 4, lines 12-17; page 10, line 23 - page 14, line 7; page 16, lines 16-24 * ---	1,2,5,7	C 10 M 129:08 C 10 M 129:16 C 10 M 129:72 C 10 M 149:06 ) C 10 N 30:02
D,A	EP-A-0 338 672 (TEXACO DEVELOPMENT CORP.) * Claims 1,7-10 * ---	6	
A	US-A-2 833 719 (W.L. VAN HORNE) * Claim 1 * ---	3,4	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,A	EP-A-0 306 290 (EXXON CHEMICAL PATENTS) * Page 4, lines 26-47; claims 1,5,9,12,23 * -----	1,2,5,7	C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06-02-1990	Examiner HILGENGA K.J.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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